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(54) Title: CERAMIC WITH ZIRCON COATING

(57) Abstract

An article comprises a silicon–containing substrate and a zircon coating. The article can comprise a silicon carbide/silicon (SiC/Si) substrate, a zircon ($ZrSiO_4$) intermediate coating and an external environmental/thermal barrier coating.

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CERAMIC WITH ZIRCON COATING

This invention was made with government support under Contract No. NAS3-26385 awarded by NASA. The government may have certain rights in the invention.

BACKGROUND OF THE INVENTION

The invention relates to a composition that includes a silicon-containing substrate and a zircon coating.

Silicon-containing substrates are proposed for structures used in high temperature applications, such as in heat exchangers and advanced internal combustion engines. For example, silicon-based composite ceramics have been proposed as materials for applications in combustors for supersonic commercial airplanes. In many of these applications, the silicon-containing substrates are subjected to highly corrosive environments such as oxidative or reducing atmospheres and environments containing salts, water vapor or hydrogen. Silicon-containing substrates exhibit poor oxidation resistance and they may recede and lose mass under water-containing environments because of the formation of volatile species, such as silicon hydroxide [$Si(OH)_4$]. Hence, it is necessary to apply external environmental/thermal barrier coatings to these materials to provide protection from environmental attack at elevated temperatures.

Although an external environmental/thermal barrier coating is capable of preventing silicon-containing substrate materials from being in direct contact with the environment, typically the external coating is an oxide that has a high coefficient of thermal expansion (CTE). The difference between the coefficient of expansion (CTE) of the silicon-containing substrate and the coeffcient of thermal expansion (CTE) of the external environmental/thermal barrier coating can result in high stress and lead to coating failure. Further mullite, which is used as an intermediate bond coating between a silicon-containing substrate and an oxide external nvironmental/thermal coating, tends to crack because of the coeffieient of themal expansion (CTE) mismatch with a silicon carbide/silicon (SiC/Si) substrate. These cracks are detrimental to the function of the ceramic coating because they serve as fast transport paths for oxidizing and corrosive species to cause severe oxidation and corrosion at interface with the substrate. Additionally, cracks in the coating concentrate stresses. The cracks apply shear and tensile forces on the substrate to cause substrate fractures.

Thus, there is a need to provide a coating to a silicon-containing substrate that reduces stress and cracks in a ceramic composite.

SUMMARY OF THE INVENTION

The present invention provides a coating that reduces thermal expansion mismatch with a silicon-containing substrate and that can be applied as an intermediate layer or as an external coating in applications where water vapor is absent. The invention is an article that comprises a silicon-containing substrate and a zircon coating.

In another aspect, the invention relates to a method of forming an article, comprising forming a silicon-containing substrate and applying a zircon coating

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph illustrating comparative coefficients of thermal expansion (CTE's) for mullite, silicon carbide (SiC), silicon (Si) and zircon ($ZrSiO_4$);

FIG. 2 is a photomicrograph of a silicon carbide (SiC) fiber-reinforced silicon carbide/silicon (SiC/Si) matrix composite processed by silicon melt infiltration coated with a zircon coating and yttria-stabilized zirconia external coating; and

FIG. 3 is a photomicrograph of the sam composit .

DETAILED DESCRIPTION OF THE INVENTION

According to the invention, a coating composition comprising zircon is applied to a silicon-containing substrate to provide a coating with a coefficient of thermal expansion that approaches the coefficient of thermal expansion of the silicon-containing substrate.

For an infinite coating on a rigid substrate (very much thicker than the coating) stress in the coating due to thermal expansion mismatch (σ_c) is given by the formula:

$$\sigma_c = -2G_c(\alpha_c - \alpha_s)\Delta T((1+V_c)/(1-V_c)) \qquad (1)$$

where G_c is the shear modulus of the coating. The coefficient of thermal expansion (CTE) of a coating can be designated α_c and the coefficient of thermal expansion (CTE) of a substrate designated α_s. ΔT is the temperature difference to which the coating and substrate are subjected and V_c is the Poisson's ratio of a coating, which is the ratio of transverse contracting strain to elongated strain. In most cases, equation (1) is applicable to coatings on silicon-containing substrates and ceramic composites. Hence, stress generated in a coating is directly proportional to the difference between the coefficient of thermal expansion (CTE) of the coating {α_c) and the coefficient of thermal expansion (CTE) of the substrate {α_s).

Figure 1 shows a comparison of the linear thermal expansion of mullite, zircon, silicon carbide and silicon as a function of temperature. Mullite has a higher thermal expansion than either silicon carbide (SiC) or silicon (Si). Zircon has a thermal expansion closer to those of both silicon (Si) and silicon carbide (SiC). Therefore, the stress in zircon due to thermal expansion mismatch is lower than that in mullite. The lower coefficient of thermal expansion (CTE) of zircon than that of silicon carbide (SiC) results in a compressive stress in the zircon coating during cooling. The compressive stress decreases the likelihood of coating cracking as zircon has a higher compressive strength than tensile strength.

Zircon comprises $ZrSiO_4$ or $ZrO_2 \cdot SiO_2$. It has an incongruent melting temperature of about 1680°C. Hence, it is adequate for most high temperature applications. Additionally, zircon has other advantages. A thin layer of silicon oxide (SiO_2) is formed on the surface of silicon (Si) and silicon-containing substrates due to the oxidation of silicon. Zirconia or one of various silicates can be used with the substrate as a water-resistant external coating. In these instances, a zircon intermediate coating has good chemical compatibility with both the underlying substrate and the external coating.

Suitable silicon-containing substrates include silicon carbide (SiC) and silicon nitride (Si_3N_4). The substrate can be a monolith or composite. A composite can comprise a reinforcing fiber, particulate or whisker and a silicon-based matrix. The matrix can be processed by melt infiltration (MI), chemical vapor infiltration (CVI) or other technique. Exemplary substrates include a monolithic silicon carbide (SiC) and silicon nitride (Si_3N_4), a silicon carbide (SiC) fiber-reinforced silicon carbide (SiC) matrix composite, carbon fiber-reinforced silicon carbide (SiC) matrix composite, and a silicon carbide (SiC) fiber-reinforced silicon nitride (Si_3N_4) composite. The preferred substrate comprises a silicon carbide (SiC) fiber-reinforced silicon carbide/silicon (SiC/Si) matrix composite processed by silicon melt infiltration.

Also suitable as silicon-containing substrates are silicon metal alloys. These alloys include niobium silicon alloys, molybdenum silicon alloys and the like.

The zircon coating can be applied to the substrate by chemical vapor deposition (CVD), thermal spray or by solution techniques such as sol-gel, slurry coating or colloidal suspension coating. Preoxidizing the silicon-containing substrate may be employed to improve adhesion of the zircon layer . A zirconia phase stabilizer, such as yttria (Y_2O_3), magnesia (MgO) or calcia (CaO) may be added to the zircon starting composition to stabilize the cubic phase and prevent volumetric changes while allowing the conversion to zircon to take place. A post-spray annealing process at appropriate temperatures (1100 to 1350 C) may also be used to help the coating material reach an equilibrium state to improve its stability. Materials of different coefficients of thermal expansion (CTE's), such as zirconia (ZrO_2), alumina (Al_2O_3), cordierite ($2MgO \cdot 2Al_2O_3.5SiO_2$) and/or fused silica ($SiO_2$), may be added to the zircon to adjust its thermal expansion in case a better match with a substrate is desired. A constituent starting powder of the coating and stabilizer and/or modifier may be premixed through a vigorous mechanical process, such as ball milling, to provide interlocking of the powders and prevent segregation of phases due to density differences. For the same purpose, a sol-gel or colloidal process may be employed to coat the particles of one constituent with another.

The zircon coating of the invention can be used as an external coating in applications where water vapor is absent or as an intermediate layer with an external environmental/thermal barrier coating. The thickness of the zircon coating is determined by the application and the materials of the substrate and external coating. When the zircon coating is applied as an external barrier, it should completely cover the substrate. In this application, the coating is typically applied as a plasma deposited coating to a thickness between about 1 to about 20 mils (25 to 500 microns), preferably between about 2 to about 10 mils (50 to 250 microns). For applications where the zircon coating serves as a bond layer, its thickness can be determined by the CTE mismatch between the substrate and the external barrier coating and the magnitude of stresses generated as a result of the CTE mismatch. Typically for plasma deposited coatings, the thickness is between about 1 to 10 mils (25 to 250 microns), preferably about 2 to 5 mils (50 to 125 microns).

Suitable external barrier coatings in the zircon bond coat application comprise an oxide such as yttria-stabilized zirconia, scandia-stabilized zirconia, calcia-stabilized zirconia or magnesia-stabilized zirconia. Alumina and alumina silicates such as barium strontium aluminosilicate and calcium aluminosilicate are also typical external coating materials.

Preferably, a zircon coating is applied as an intermediate layer to a composite that comprises a silicon carbide/silicon (SiC/Si) substrate and a yttria-stabilized zirconia external environmental/thermal barrier coating. The following example is illustrative of the invention.

EXAMPLE

A zircon coating was sprayed by air plasma onto a ceramic composite substrate. The coating was deposited using a 23KW plasma gun, argon (Ar) as primary gas and hydrogen as secondary gas. The plasma gun to substrate distance was 1.5 inch. The ceramic substrate was a silicon carbide (SiC) fiber-reinforced silicon carbide/silicon (SiC/Si) matrix composite processed by silicon melt infiltration. The zircon coating was covered with a yttria-stabilized zirconia coating.

FIG. 2 and FIG. 3 are photomicrographs of the resulting composite and show that a zircon coating can be deposited by plasma spray and that the resultant coating is free of large cracks.

CLAIMS

What is claimed:

1. An article, comprising a silicon-containing substrate and a zircon coating.

2. The article of claim 1, wherein said zircon comprises $ZrSiO_4$ or $ZrO_2 \cdot SiO_2$.

3. The article of claim 1, wherein said substrate comprises silicon carbide (SiC) or silicon nitride (Si_3N_4).

4. The article of claim 1, wherein said substrate is a composite comprising a silicon-based matrix and a reinforcing fiber, particulate or whisker.

5. The article of claim 1, wherein said substrate comprises a monolithic silicon carbide (SiC) or a monolithic silicon nitride (Si_3N_4).

6. The article of claim 1, wherein said substrate comprises a silicon carbide (SiC) fiber-reinforced silicon carbide (SiC) matrix composite, a carbon fiber-reinforced silicon carbide (SiC) matrix composite or a silicon carbide (SiC) fiber-reinforced silicon nitride (Si_3N_4) composite.

7. The article of claim 1, wherein said substrate comprises a silicon carbide (SiC) fiber-reinforced silicon carbide/silicon (SiC/Si) matrix composite processed by silicon melt infiltration.

8. The article of claim 1, wherein said zircon coating comprises a zirconia phase stabilizer.

9. The article of claim 8, wherein said phase stabilizer comprises yttria (Y_2O_3), magnesia (MgO) or calcia (CaO).

10. The article of claim 1, wherein said zircon coating comprises a modifier that imparts a closer coefficient of thermal expansion (CTE) match between said zircon coating and said substrate.

11. The article of claim 10, wherein said modifier comprises zirconia (ZrO_2), alumina (Al_2O_3), cordierite ($2MgO \cdot 2Al_2O_3.5SiO_2$), fused silica ($SiO_2$), silicon (Si) or mixture thereof.

12. The article of claim 1, wherein said zircon coating is an external coating for application in an environment free from water vapor.

13. The article of claim 1, further comprising an external environmental/thermal barrier coating.

14. The article of claim 1, further comprising an oxide external environmental/thermal barrier coating.

15. The article of claim 14, wherein said oxide external environmental/thermal barrier coating is selected from the group consisting of yttria-stabilized zirconia, scandia-stabilized zirconia, calcia-stabilized zirconia, magnesia-stabilized zirconia and mixtures thereof.

16. The article of claim 13, wherein said external environmental/thermal barrier coating is an alumina or alumina silicate.

17. The article of claim 13, comprising a silicon carbide/silicon (SiC/Si) substrate and a yttria-stabilized zirconia external environmental/thermal barrier coating.

18. The article of claim 1, shaped into an engine part.

19. The article of claim 13, shaped into an engine part.

20. An article of manufacture, comprising a part coated with the composition of claim 1.

21. An article of manufacture, comprising a part coated with the composition of claim 13.

22. The article of manufacture of claim 21, wherein said part is a gas turbine engine part or an aircraft engine part.

23. A method of forming an article, comprising;

forming a silicon-containing substrate; and

applying a zircon coating onto said substrate.

24. The method of claim 23, further comprising applying an external environmental/thermal barrier coating onto said zircon coating.

25. The method of claim 24, wherein said substrate has a lower coefficient of thermal expansion than the coefficient of thermal expansion of said external environmental/thermal barrier coating, comprising applying said zircon coating onto said substrate to reduce thermal stress between said substrate and said external environmental/thermal barrier coating.

26. The method of claim 23, comprising applying said zircon coating onto said substrate by chemical vapor deposition (CVD), thermal spray, sol-gel, slurry coating or colloidal suspension coating.

27. The method of claim 23, comprising preoxidizing said substrate to improve adhesion of said zircon coating.

28. The method of claim 23, further comprising annealing said zircon coating to improve its stability.

29. The method of claim 23, comprising mixing a powder of zircon with a stabilizer or modifier and applying a resulting coating to said silicon-containing substrate.

30. The method of claim 29, comprising mixing said powder and stabilizer or modifier by ball milling.

31. The method of claim 24, further comprising applying said external environmental/thermal barrier coated composition to a part to form an article of manufacture.

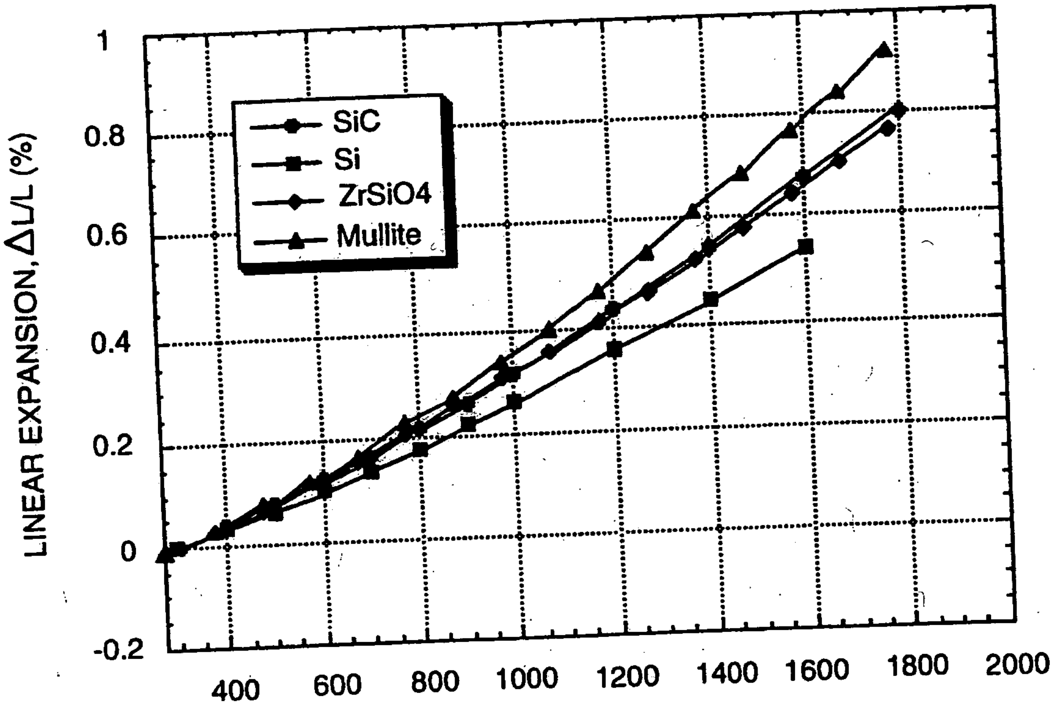
LINEAR EXPANSION, ΔL/L (%)
1
0.8
0.6
0.4
0.2
0
-0.2
400
600
800
1000
1200
1400
1600
1800
2000
TEMPERATURE
SiC
Si
ZrSiO4
Mullite

FIG. 1

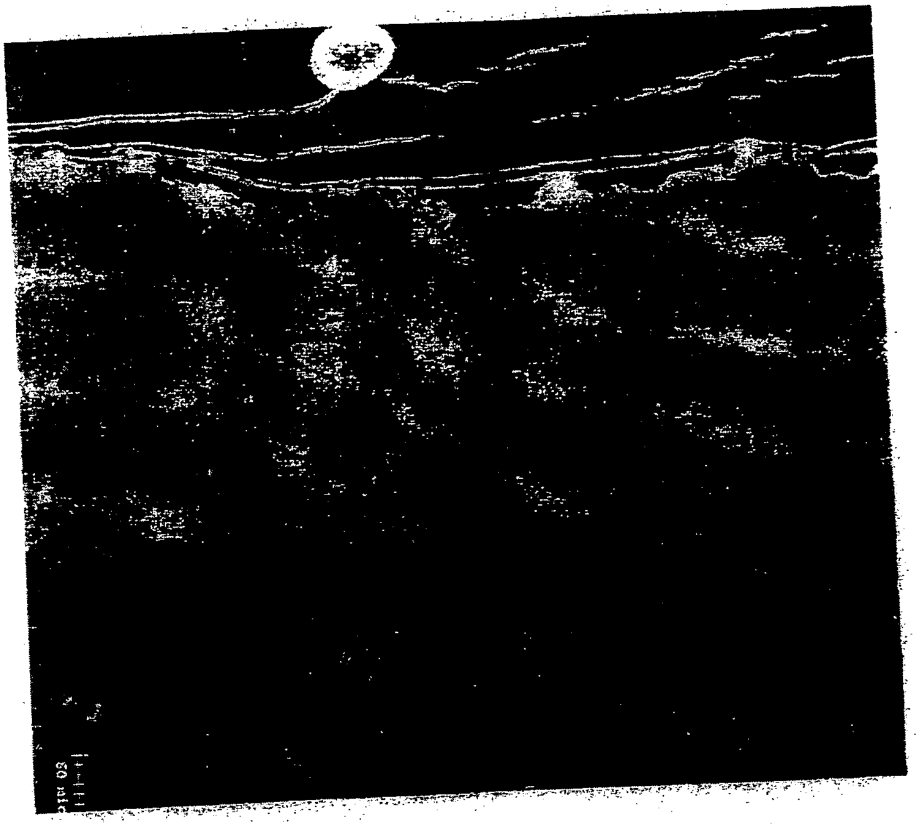

FIG. 2

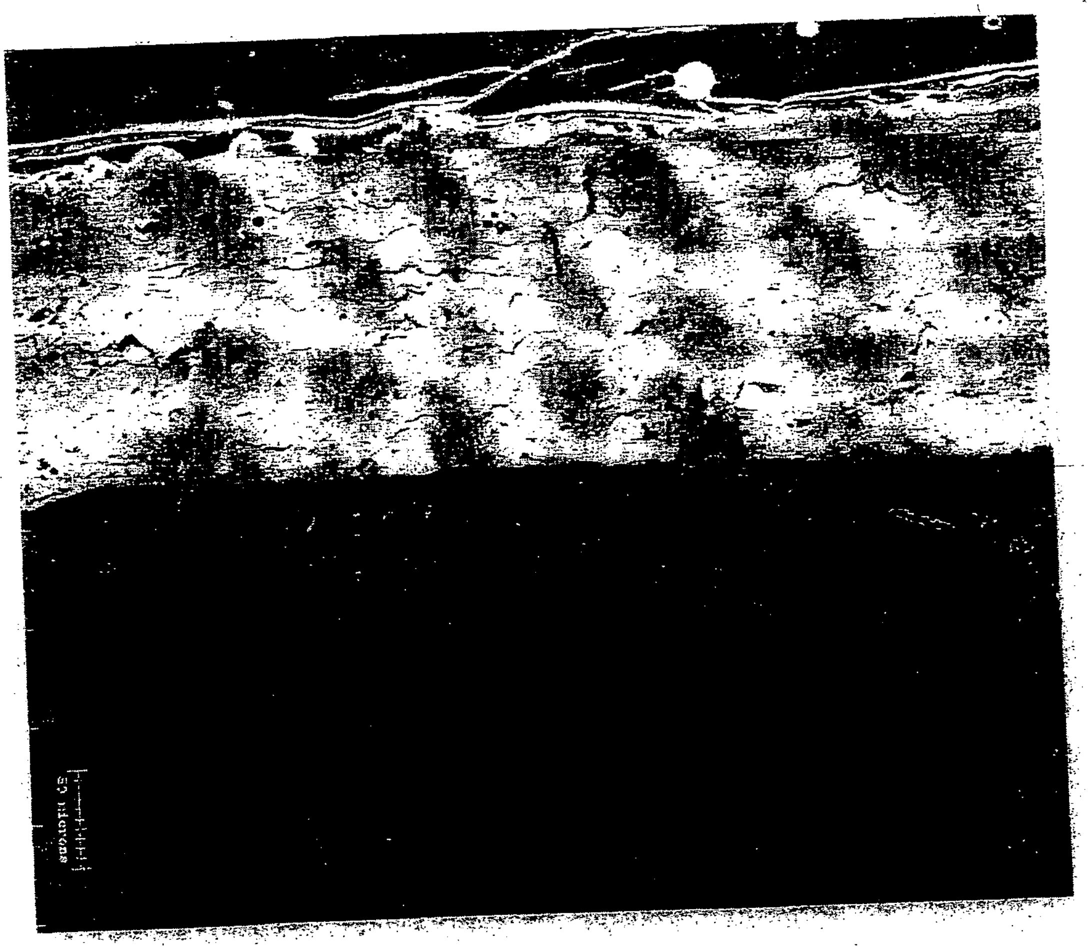

FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/10478

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B41/87

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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